SOME PRELIMINARY MEASUREMENTS OF FREE RADICAL FORMATION
IN POLYMERS UNDER STRESS

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ABSTRACT

It is proposed to present some initial observations on the use of electron paramagnetic resonance to detect the number of free radicals formed in polymeric materials due to the application of tensile stress. A summary of pertinent theoretical background, including the pioneer work of Zhurkov (1) will be followed by our initial results showing the signatures and decay rates obtained in two materials, drawn Nylon and Solithane 113, for three types of damage to the specimens -- crushing, radiation, and stretching.

INTRODUCTION

For the past several months we have been conducting a study of the microscopic failure mechanisms in polymers using an electron paramagnetic resonance (EPR) spectrometer. Zhurkov first demonstrated in 1964 that if a polymer was stretched in tension, the force fields between adjacent atoms on the microscale would also be altered, and in some cases sufficiently so that the chemical bonds would be broken, thus giving rise to free radicals at the broken chain ends which could be sensed by EPR techniques somewhat analogous to the birefringent effect which likewise is induced by mechanical stress giving rise to optical interference. The electromagnetic absorption, which increases with increasing load and increasing free radical production, are recorded to the spectrometer. The purpose of our studies has been to investigate the extent to which quantitative correlation can be made between the initiation of micro-flaws and the applied gross stress.

BACKGROUND INFORMATION

The following brief description of EPR spectroscopy is purposely oversimplified. It is believed sufficient, however, to explain the essential features of our investigation.

EPR deals with systems of elementary particles which have a net electronic moment (unpaired electron spins). Basically, it is another type of absorption spectroscopy with principles and applications somewhat similar to those of optical spectroscopy. Its physical basis is perhaps best understood by first considering the case of a free electron. Associated with the electron spin is a magnetic moment given by

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$$\bar{\mu} = -g\beta\bar{s} \tag{1}$$

where g is the spectroscopic split.ing factor, β is the Bohr magneton, and $\bar{s}$ is the spin vector. In the absence of an external magnetic field the energy is the same for both + and − spins. When subjected to an external magnetic field, however, the energy is split into two levels as shown below.
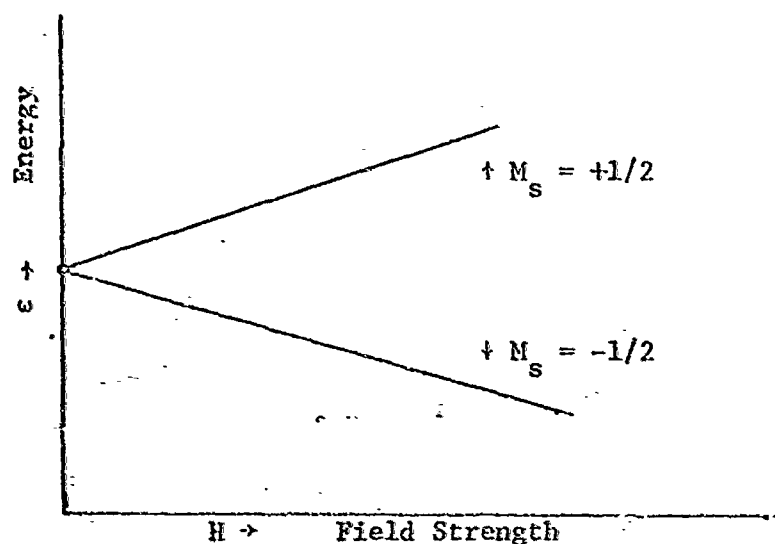

Figure 1. Spectroscopic Spilling Factor for a Free Electron

In Figure 1, H is the magnetic spin field in gauss and M_s is the spin quantum number which is restricted to values of +1/2 and −1/2. The populations of the two energy levels are given by Boltzmann statistics. An excess of free electrons will reside in the "gr'und state," i.e. M_s = −1/2, corresponding to the lower energy. However, should electromagnetic energy be present at frequency ν such that hν is equal to the energy difference between the two levels (h is Planck's constant), the electron can be pumped to the higher state. When these electrons relax back to the ground state giving up their energy to the lattice, a net energy absorption takes place. The resonant condition is given by

$$h\nu = g\beta H \tag{2}$$

For a free electron in a one gauss field the resonance should occur at ν = 2.8 megacycles. Most EPR work is done at X-band frequencies, i.e. approximately 10^4 megahertz. The Varian E-3 equipment in use at the University of Utah which was purchased under our NASA grant is of this type. With this equipment it is possible to determine concentrations as small as approximately 10^{11} ΔH spins where ΔH is the line width in gauss for a signal to noise ratio of one. For polymeric free radicals, ΔH is typically from 1 to 100 gauss.

In very simple terms this equipment can be used to study fracture as
follows. In covalently bonded materials the valence electrons are shared
between atoms. In the bonded state the shared electrons are locked, how-
ever, into a given quantum spin state. The Pauli exclusion principle makes
it impossible for these electrons to all align with the applied magnetic
field. If the bond should be broken, e.g. during fracture, there is a
tendency for the now freed electrons to align their magnetic vectors with
the applied field. Hence if a tensile specimen is placed in the X-band
microwave resonant cavity and any bonds broken as the polymer chains ex-
tend, the free radicals will, in the presence of the applied electromag-
netic field, absorb electromagnetic radiation of the appropriate frequency.
A measurement of the spectrum of this microwave absorption then gives a
measure of the free radicals resulting from the bond rupture.

In more complicated structures than single electrons, analysis of the
behavior becomes more complicated, as well as more intriguing. The shape
of the spectra including such factors as hyperfine splitting should make
it possible to determine not only how many bonds are broken but which bonds.
The electron senses not only the presence of the applied magnetic field
but is capable of electrical and magnetic interaction with the protons in
the nuclei and the electrons of the surrounding atoms. This interaction
gives rise to the "splitting" that can often be used to identify the par-
ticular free radical. More extensive descriptions of EPR, its uses, and
applications can be found in References 2 through 9.

The study of free radical chemistry is currently an extremely active
research area and EPR spectroscopy has become a standard analytical instru-
ment in this field.(7,8) Many different types of degradation processes,
including some of direct interest in solid propellant aging, have been
investigated. Such processes as thermal degradation, anionic degradation,
ultraviolet and x-ray irradiation, electron and neutron bombardment, etc.
have been studied quite extensively with EPR. Strangely however, the EPR study
of mechanical degradation (i.e. the breaking of polymeric bonds by mechan-
ical processes) seems to have been heretofore completely neglected in this
country. The feasibility of such studies was first demonstrated by S. N.
Zhurkov, corresponding member of the USSR Academy of Sciences (1,10,11,12).
In his study he correlated the phenomenological description of the fracture
of solids with microscopic studies of bond breakage in polymeric materials.
He reported that for Nylon 6 the rate of formation of free radicals is an
exponential of the applied tensile stress.

$$\frac{dc}{dt} = \gamma \, \exp(\beta \sigma) \tag{3}$$

where c is the concentration of free radicals, γ a constant, and β is the
rate constant for the process. He further reported observations that the
lifetime of solids varies with the applied tensile stress σ and the tem-
perature T as:

$$\tau = \tau_o [\exp(U_o - \alpha\sigma)/KT] \tag{4}$$

where τ_0 coincides with the reciprocal of the natural oscillation frequency of atoms in solids, U_0 is a measure of the strength of the chemical bond, and α is a coefficient which accounts for the overstress on a bond as compared to the average stress in a specimen. This formulation is of great interest and utility to both the solid state scientist and the materials engineer. It implies a kinetic concept of fracture in which a bond activation energy of magnitude $(U_0 - \alpha\sigma)$ is overcome by thermal oscillation in the solid and the broken bonds accumulate, at given stress, according to a first-order rate law.

Zhurkov next presented evidence to the effect that a direct experimental confirmation of this molecular viewpoint can be obtained through the use of EPR techniques in the investigation of mechanical stressed polymers. A comparison of Equations 3 and 4 show that if bond breakage unambiguously determines the fracture lifetime of polymers, α and β in Equations 3 and 4 should be equal and in that case at constant temperature

$$\tau_1 \frac{dc}{dt} = \text{constant} \tag{5}$$

or

$$\ln \frac{dc}{dt} = \ln(\text{constant}) - \ln\tau_1 \tag{5a}$$

Zhurkov reported that this relation was valid for Nylon 6.

The Zhurkov formulation is so elegant and sweeping in its implications that the authors felt it merited careful verification and further investigation by researchers in this country.

SUMMARY OF CURRENT INVESTIGATION

As was to be expected there were several delays in obtaining the first data. By and large these difficulties are not pertinent here and a brief chronology of our work to date will be presented. First some accessory equipment was required. In addition to a Varian E-3 spectrometer which is the basic instrument employed on the project, a loading system and recording instrumentation has been designed and partially assembled. When completed, the loading system will be capable of constant load, constant strain rate, and constant displacement as well as various programmed loadings. The equipment includes a variable temperature controller capable of maintaining temperatures from -190°C to 300°C and an oscillograph recorder capable of recording up to twelve variables simultaneously.

We note first that the spectrum for a particular free radical is essentially the same regardless of the manner in which it is produced. One of our first tasks therefore was to compare and calibrate our experimental set-up with respect to other types of degradation currently reported in the

literature. One of the most popular interests pertains to the free
radicals produced by γ-irradiation. (13-19) We also conducted tests
on several different polymeric materials subjected to varying amounts
of irradiation from a Co^{60} source. Particular attention has been devoted
to the annealing of these spectra at different temperatures. This will
be useful for comparison (and extrapolation to zero time) with the frac-
ture data. Figures 2 and 3 show typical spectra of irradiated polymers.

As a second type of specimen also originally tried by Zhurkov, we
have used a polymeric solid ground to a powder. This mechanical breaking
of the bonds will create free radicals, at least until the free chain ends
are neutralized by other radicals present in the surrounding environment.
One might expect this process to relate to irradiation-produced degradation
in that both processes would be expected to break polymeric bonds rather
indiscriminately, i.e. there should be as much tendency to sever a strong
bond as a weak one. Several different types of polymers were ground in
various atmospheres (air, nitrogen, helium, hydrogen) at both liquid ni-
trogen and room temperatures.* The spectra obtained from these powders
are now being correlated with those obtained from irradiated samples.
The lifetime of free radicals produced by grinding was found to be more
highly atmosphere and temperature sensitive than irradiated samples. The
presence of oxygen at room temperature resulted in a lifetime which was
on the order of seconds while the free radical concentration could be main-
tained indefinitely in an inert atmosphere at liquid nitrogen temperature.
Typical grinding spectra are shown in Figures 4 and 5.

Next, attention was turned to our main objective — investigation of
free radical formation during tensile loading to fracture. Bundles of
drawn Nylon 6 fibers have been fractured at room temperature. Figure 6
shows a spectrum which exhibits the typical increase in free radicals with
increasing stress at approximately constant deformation rate. In a con-
stant-strain rate test the EPR signal grows noticeably as deformation
proceeds. For the constant load tests, however, we did not observe a mono-
tonic growth in the free radical concentration as was reported by Zhurkov.(1,12)
Rather, the signal tended to approach a steady-state concentration via what
seemed to be a first-order kinetic process. (Figures 6 and 7). Although
experimental work and data reduction from these tests is just beginning
and is still in progress, there appears to be a significant disparity be-
tween our work and that of Zhurkov.

In particular we feel that the matter of free radical combination,
i.e. the reformation of broken bonds merits more attention. Zhurkov's ini-
tial constant stress stud· caused him to postulate that (1) fracture is
singularly dependent on bond rupture, and (2) that this bond rupture is
given by a constant rate, stress-dependent relation

$$\dot{c} = \gamma e^{j\omega} \tag{6}$$

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* The studies are conducted at different temperatures in an attempt to
determine the kinetics of free radical migration. This will be helpful in
extrapolating back to the time of fracture.

In this case then, the number of free radical's produced by bond breakage in polymers which are present at any time would be the time integral of (6) minus the number which have disappeared or annealed, e.g. internal recombination with other chains or combination with external diffusing impurities. Figure 8, which represents the annealing in air of the free radical concentration with time after removal of the load, suggests that the annealing process obeys a first-order kinetic process. If one is then content with this simple addition to (6), there results

$$\dot{c} = \gamma e^{\beta \sigma} - (c/\tau) \tag{7}$$

in which τ is the characteristic annealing time. For a constant stress test, this model predicts the radical concentration at any time to be

$$c = \gamma \tau e^{\beta \sigma}[1 - e^{-t/\tau}] \tag{8}$$

Figure 9 which shows the early part of a free radical growth curve for a constant load test,[*] can be fit to (8) if τ is taken to be near 40 seconds. The relaxation time associated with Figure 8, however, is approximately twenty times larger than this. Even though this anomaly might be explained in terms of a stress-aided relaxation, such a mechanism is difficult to envision and it seems more likely that the relaxation term in (7) is due to some effect other than that observed in Figure 8. This criticism of the Zhurkov model is further illustrated in Figure 10, in which the radical concentration under constant load is observed to rise to some peak value and decay thereafter. This decay seems due to radical annealing effects, again forcing us to look elsewhere for a satisfactory interpretation of the second term in Equation (7).

Another even more critical test of the Zhurkov model was undertaken. A constant load was applied to the sample and maintained until the "quasi-steady state" concentration was obtained. The load was then removed and the free radical concentration allowed to anneal until no detectable EPR signal was present. The sample was then reloaded to the original load. If (6) was valid, we should obtain a spectrum similar in all details to that obtained with the first loading. As seen in Figure 11, however, such was not the case; few free radicals were formed in the second application of the load. It would seem, at least in our Nylon 6 fibers, that a given stress will break a certain number of bonds and that this stress must be increased if more bonds are to be broken.

CONCLUDING REMARKS

Finally, it is appropriate to remark upon some studies which relate to our work. First it is noted that even though Bueche (20,21) and Busse (22) agree with the general form of Zhurkov's $\sigma-\tau$ relation for creep tests, Bartenev (23) reports that isothermal creep data is better represented by an equation of the form

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[*] It should be noted that Zhurkov took especial care to attain a constant stress during loading. Our tests to date have not incorporated this refinement and its possible implication is being investigated.

$$\ln\sigma = \ln A - B\ln n \qquad (9)$$

Zhurkov himself reports deviation from his own formulation which he attributed to free radical recombination. (1) Interestingly, these deviations (a tendency at low stresses for the data not to fit a straight line on the σ-$\ln n$ plot) are the same ones which Bartenev avoids in his formulation: he found the data to fit straight lines on $\ln\sigma$-$\ln n$ plots.

Second, it appears promising to investigate a possible correlation of free radical accumulation with the NASA sponsored work being continued at the California Institute of Technology by Knauss. Knauss has been developing a rupture criterion which combines the energy-balance approach of prior theories with a theoretical description of bond breakage rates under an applied stress. (24-26) He has shown that the net rate of increase in the fraction of bonds broken due to the storage of elastic energy should be

$$\frac{a_T}{2B}\frac{d}{dt}\frac{N_2-N_1}{N_0} = -\frac{N_2-N_1}{N_0}\left[\cosh\frac{W}{NKT} + \sinh\frac{W}{NKT}\right] \qquad (10)$$

where a_T is the time-temperature shift factor and W is the average stored energy per unit volume, B a constant, N Avagadro's number, and K Boltzmann's constant. Through W, (10) allows for the past history of loading and the nature of the particular polymeric material. N_1 is the number of unbroken bonds and N_2 is the number broken at any time; $N_0 = N_1 + N_2$ is the total number of bonds in the region under consideration.

In conclusion, the authors feel that the work to date, while preliminary in nature, has demonstrated the utility of the EPR method in studying certain fracture mechanisms in polymers. Pending the satisfactory completion of our exploratory program, it appears that the technique will be of considerable help in explaining mechanically and environmentally induced fracture in solid propellant binders.

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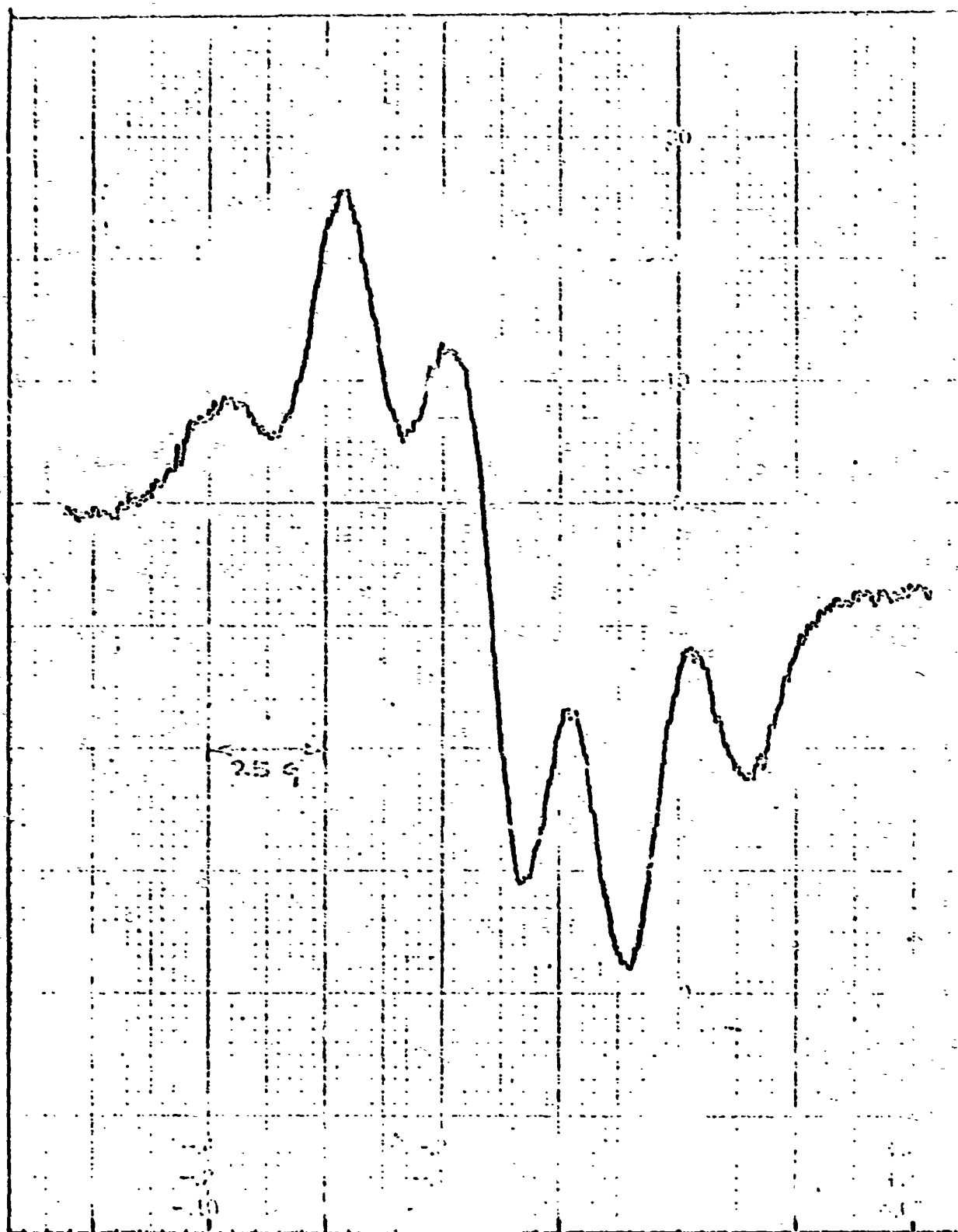
Figure 2. Nylon 6 irradiated with 20,000 rads (C_o^{60} source) at liquid Nitrogen Temperature, then Stored Five Minutes at 74°F. Spectrum Taken on Approximately 2 grams at Liquid Nitrogen Temperature.
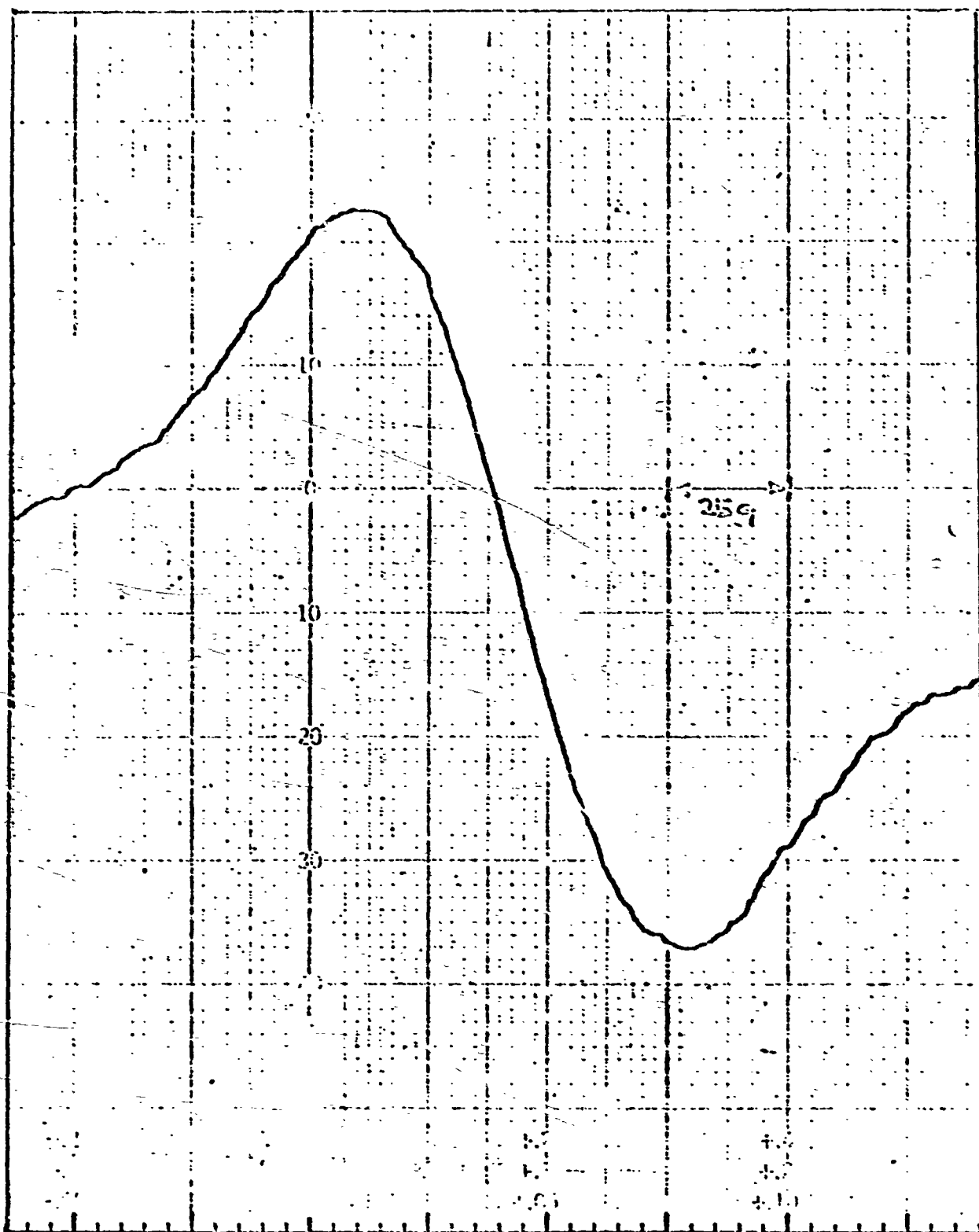
Figure 3. Solithane 113 (50-50) Irradiated with 180,000 Rads (C^{60} Source)
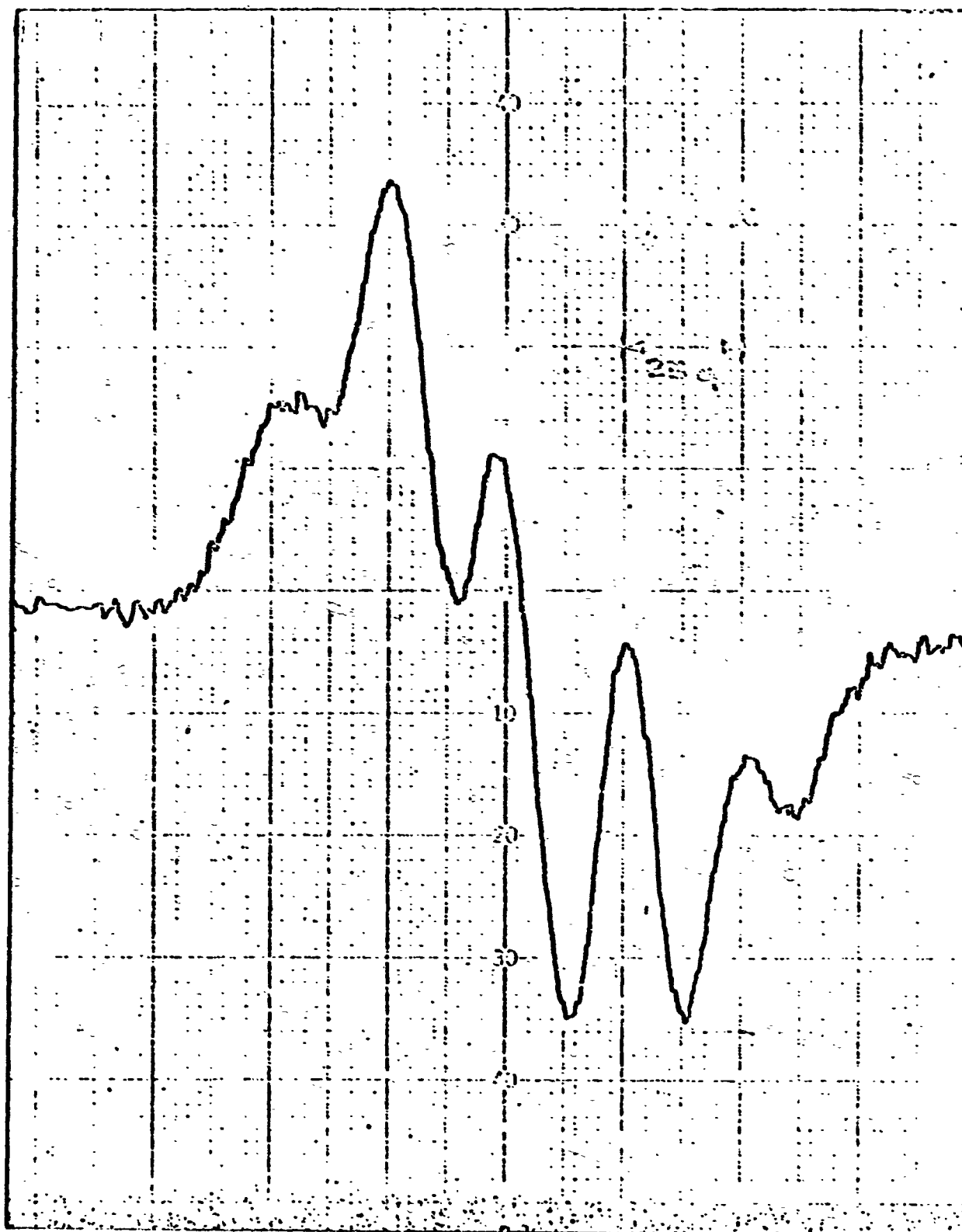At Liquid Nitrogen Temperature; Spectrum Taken at Liquid Nitrogen Temperature.

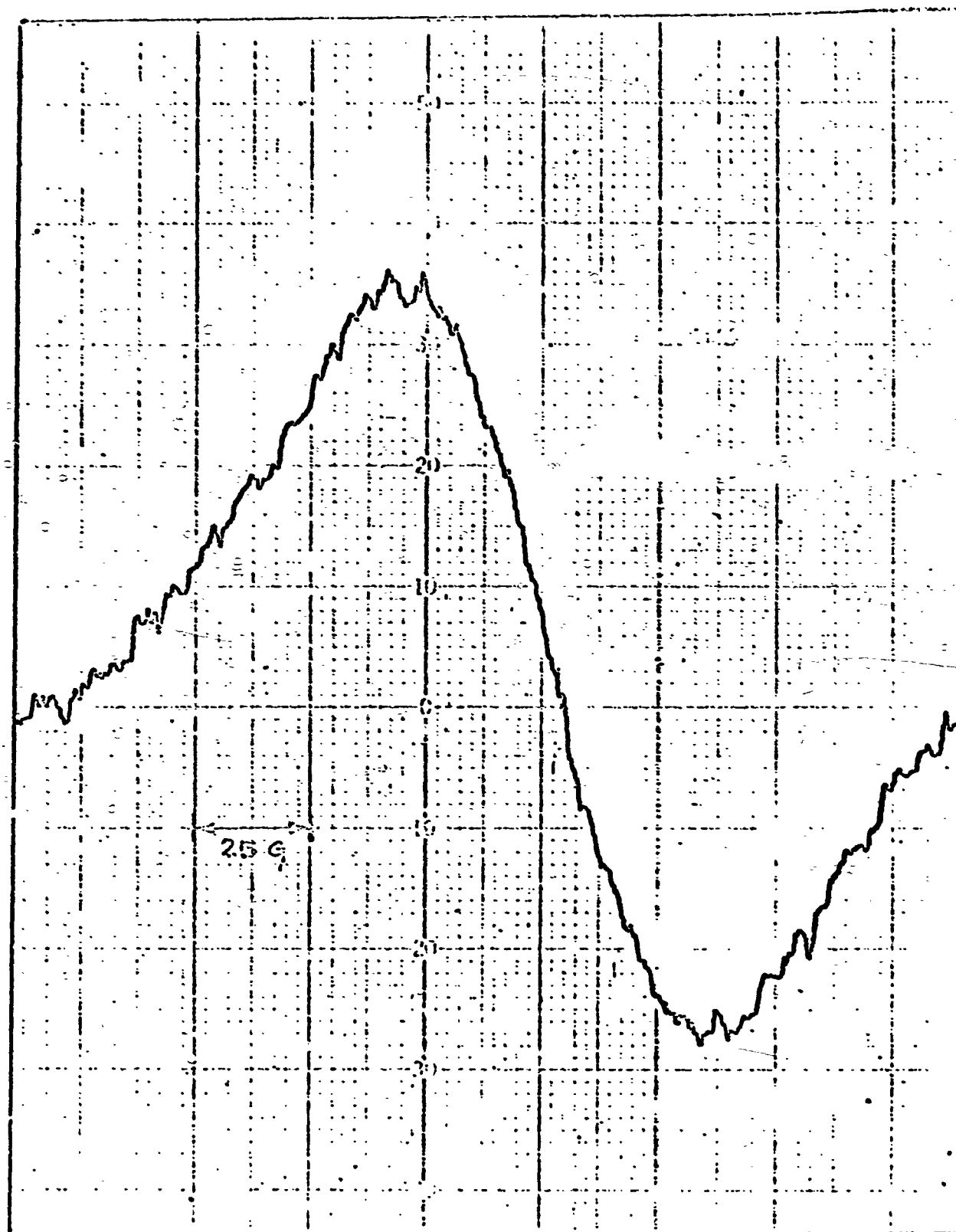**Figure 4.** Nylon 6--Mechanically Ground in N_2 Atmosphere at Liquid Nitrogen Temperature. Spectrum Taken at Liquid Nitrogen Temperature.

Figure 5. Solithane 113 (50-50) Ground to Powder in He Atmosphere at Liquid Nitrogen Temperature. Spectrum Taken at Liquid Nitrogen Temperature.
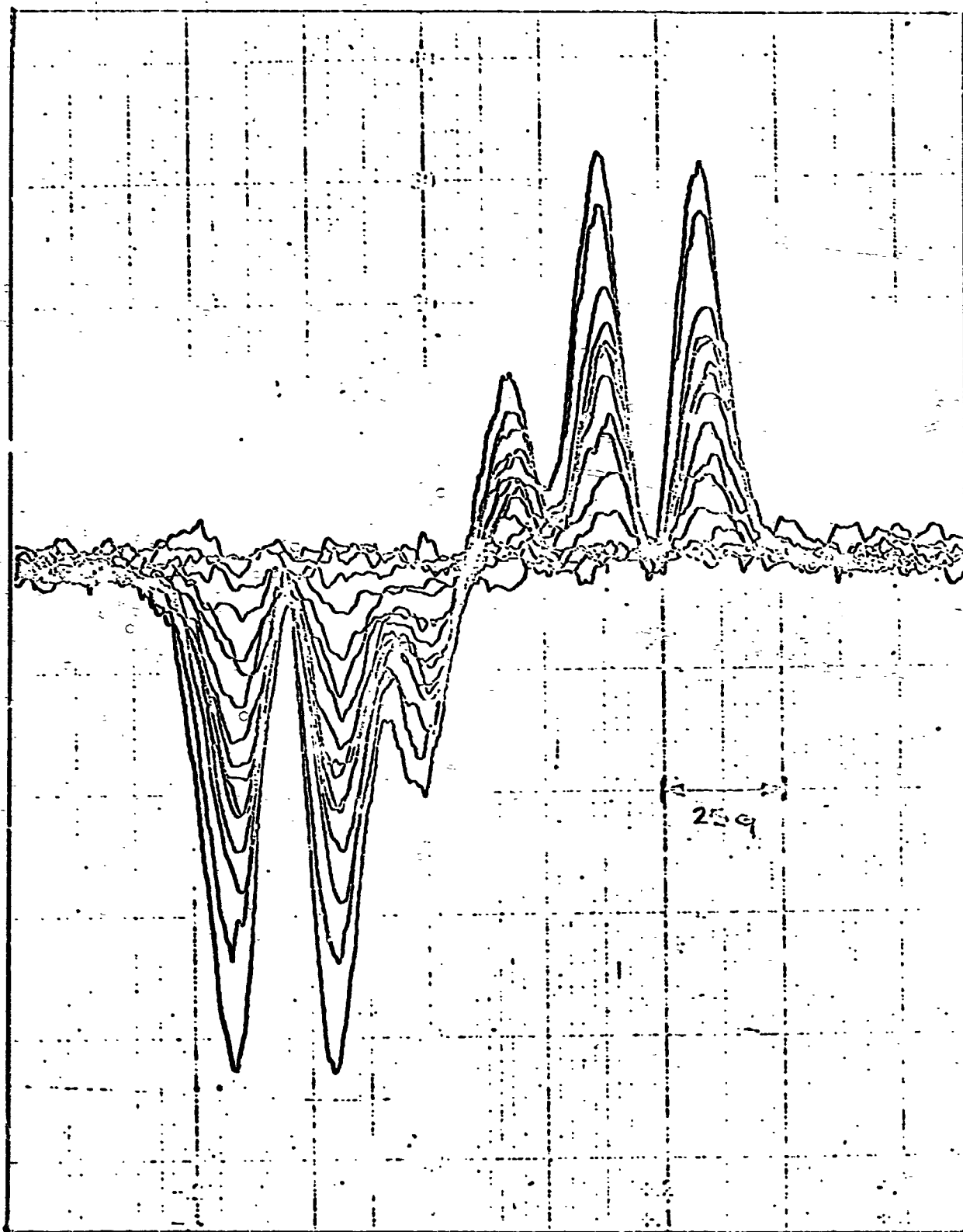
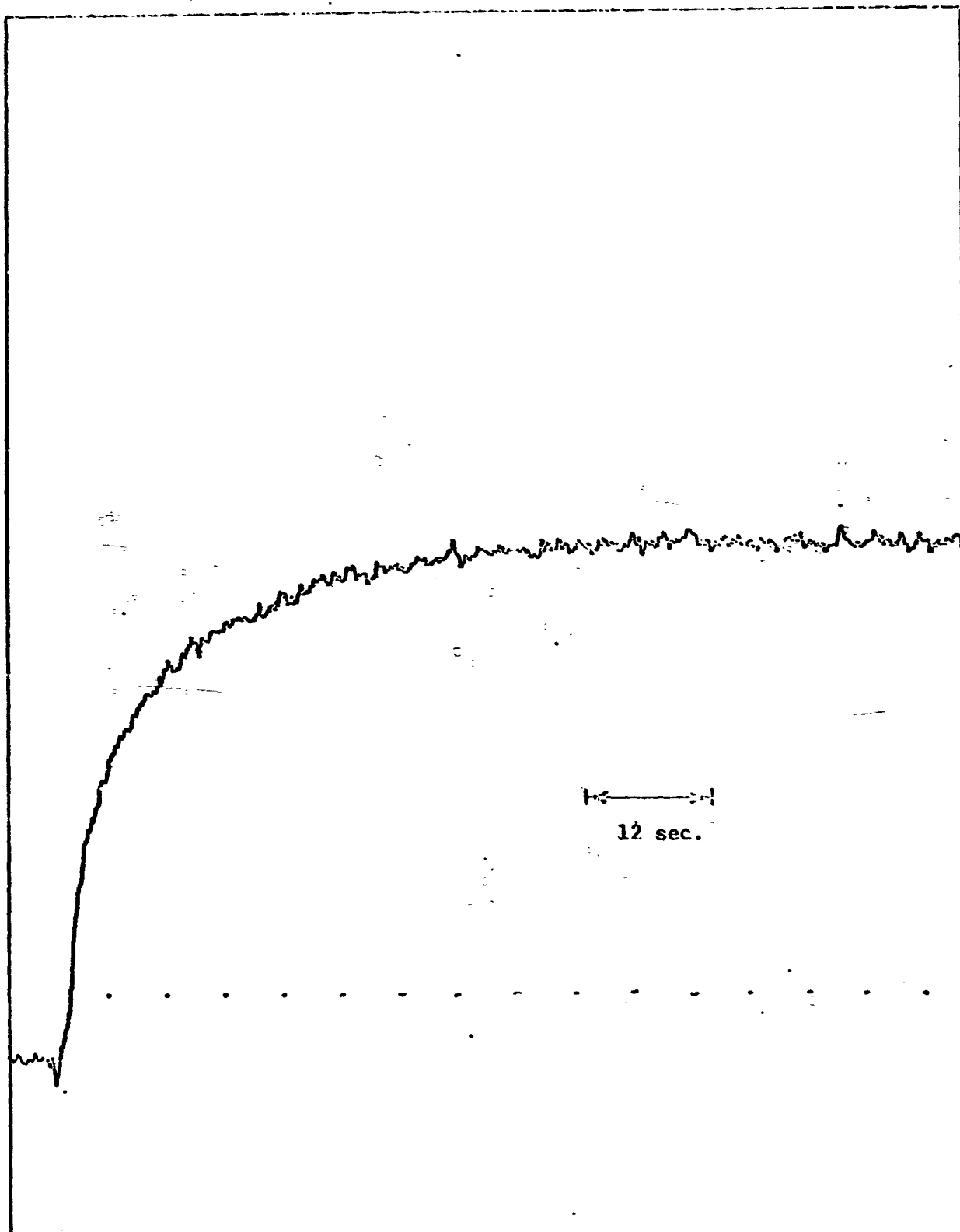**Figure 6.** Drawn Nylon 6 Fibers During Tension Test--Accumulation of Free Radicals as Load Increased.

12 sec.

Figure 7. Drawn Nylon 6 Fibers in Tension -- Accumulation of Free Radicals (Height of Absorption Peak) as a Function of Time during Constant-Load Test.
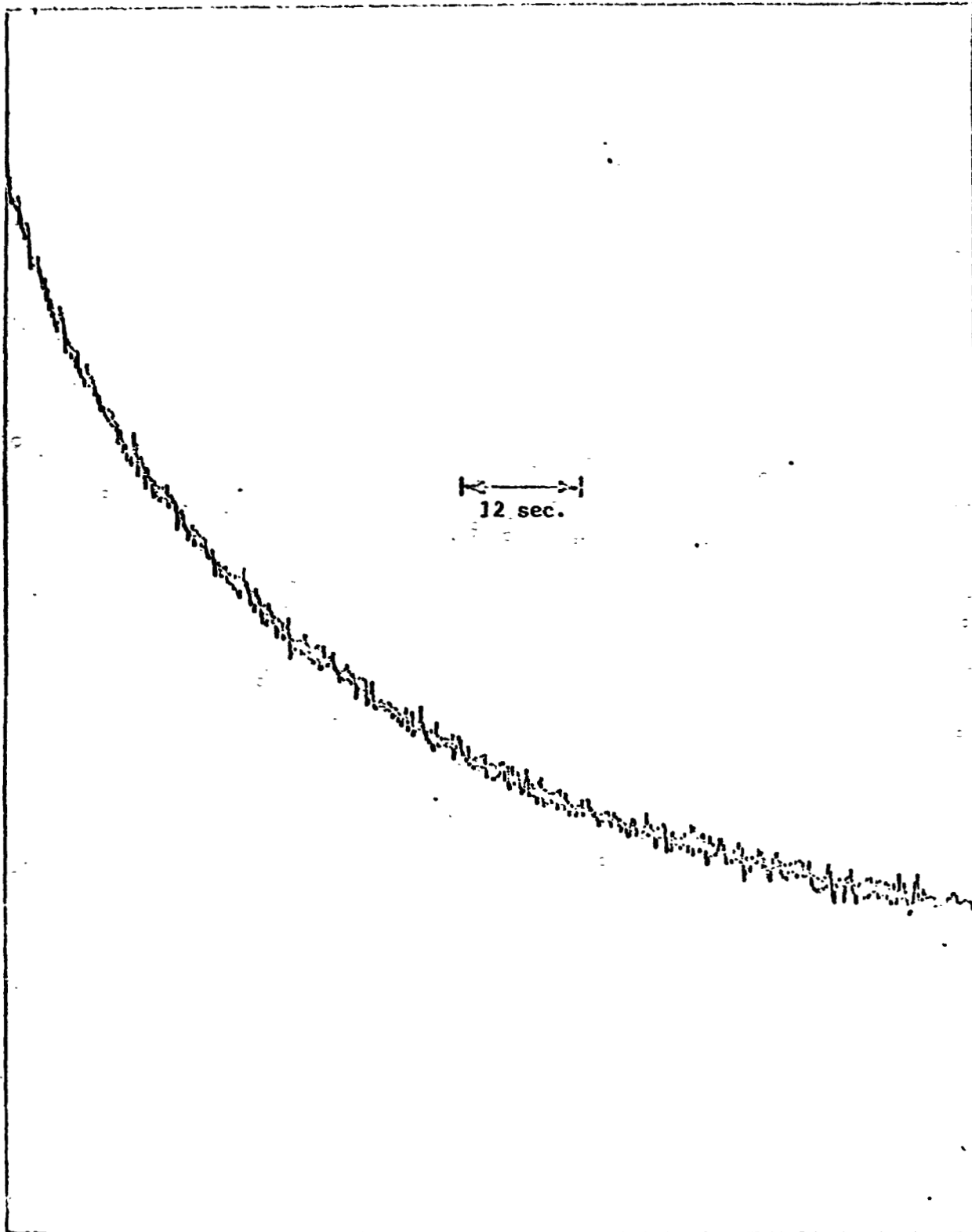
Figure 8.   Drawn Nylon 6 Fibers - Decay of Free Radical Concentration
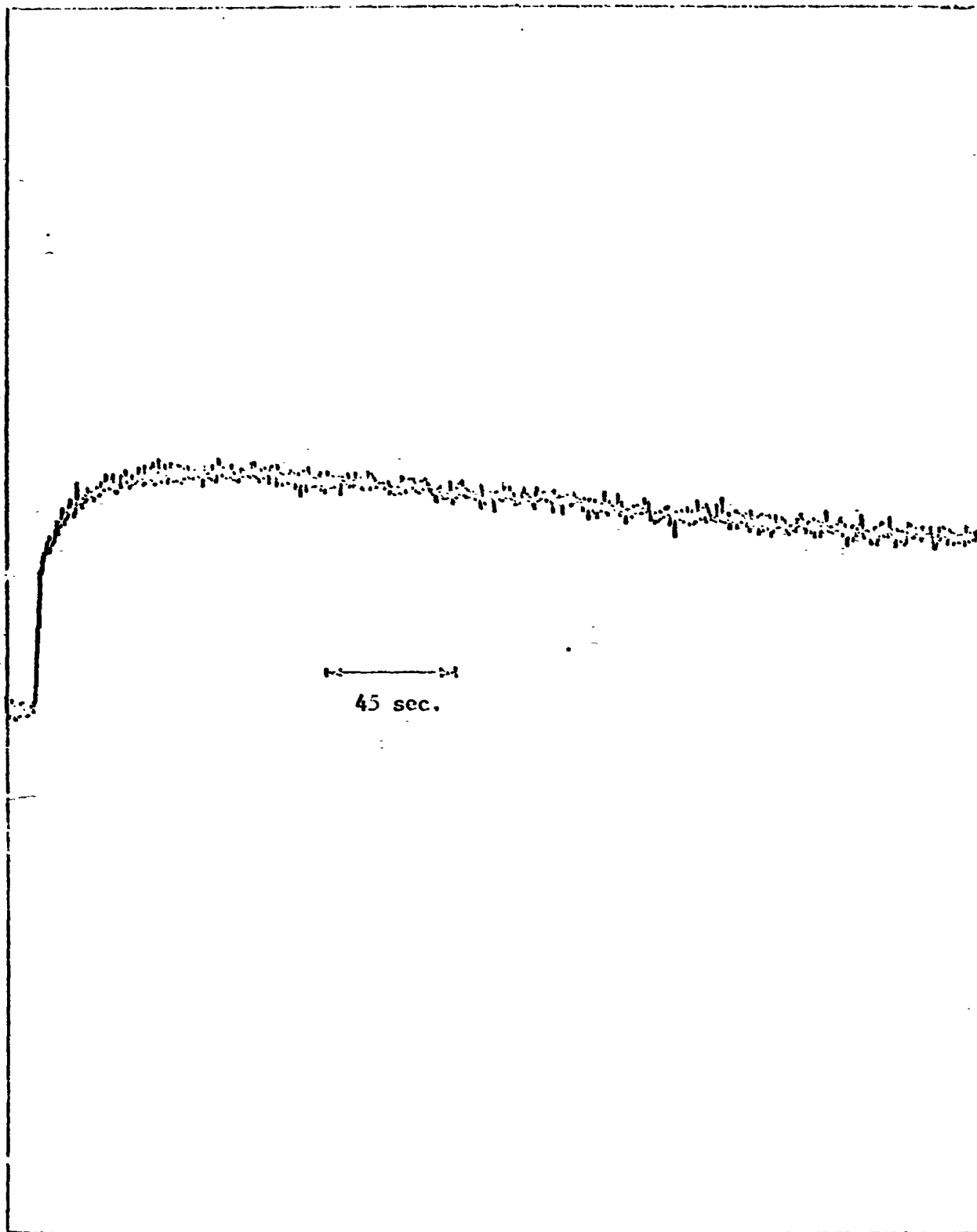with Time after Removal of Load.

45 sec.

Figure 9. Nylon 6 Fibers - Free Radical Growth during Constant-Load Test.
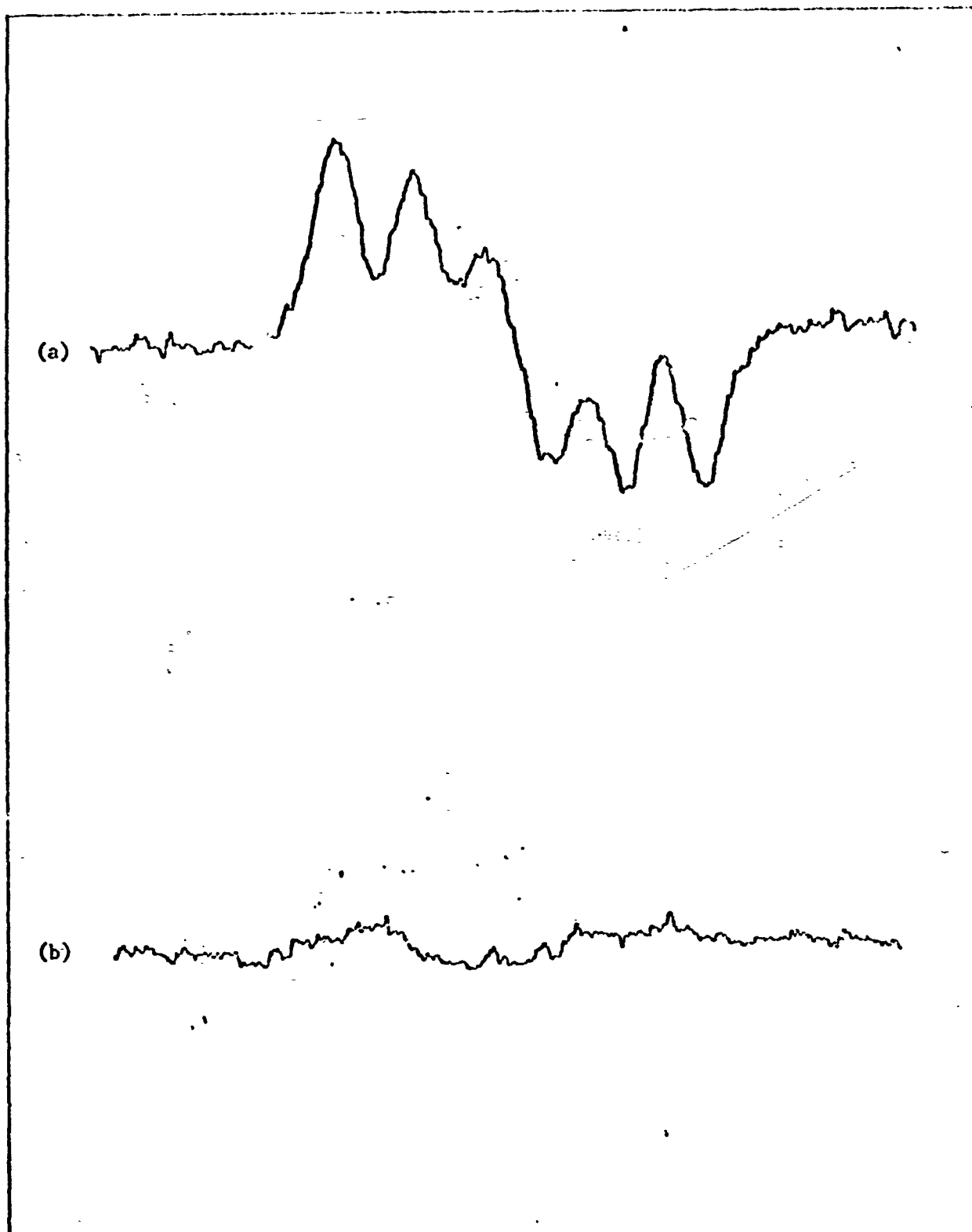
Figure 10. (a) EPR Spectrum of Nylon 6 Fibers after Loading to 80,000 psi.
           (b) EPR Spectrum after Annealing and Reloading to 80,000 psi.